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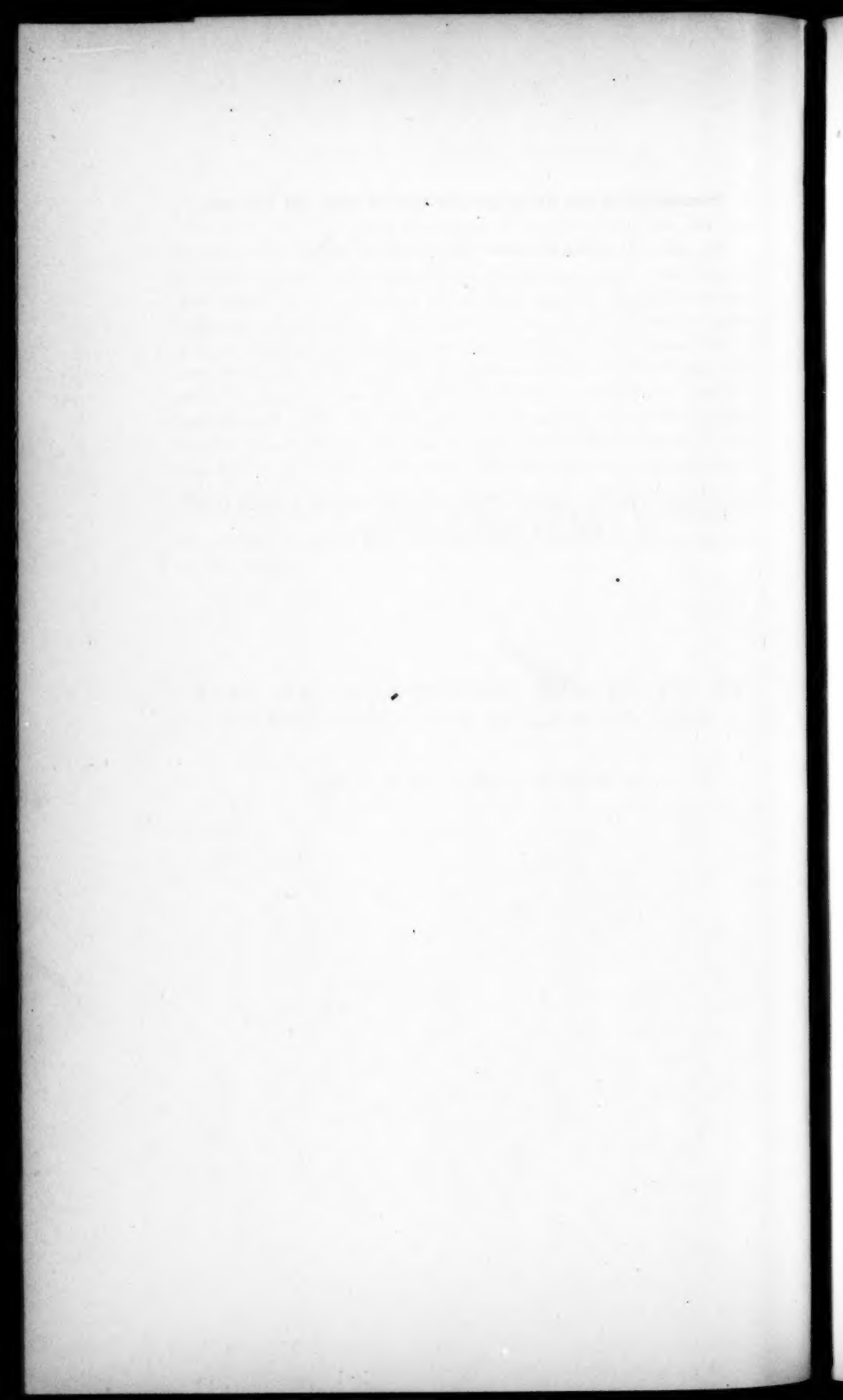
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF HARVARD COLLEGE.

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*ON THE COLORED COMPOUNDS OBTAINED FROM  
SODIC ALCOHOLATES AND PICRYLCHLORIDE.*

BY C. LORING JACKSON AND W. F. BOOS.



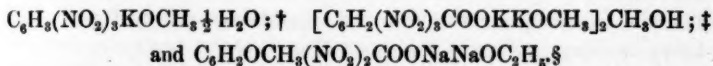
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ON THE COLORED COMPOUNDS OBTAINED FROM SODIC  
ALCOHOLATES AND PICRYLCHLORIDE.

BY C. LORING JACKSON AND W. F. BOOS.

Presented January 12, 1898.

THE work described in this paper is the continuation of a research begun by M. H. Ittner and one of us,\* about three years ago, upon the colored products of the action of sodic alcoholates on certain aromatic nitro compounds. For a statement of the work of Lobry de Bruyn and Van Leent, and of Victor Meyer, on this subject, the reader is referred to that paper.\* The first object to which we turned our attention was the isolation and analysis of more substances of this class, since only three analyses of such bodies had been published; these three analyses led to the following formulas:—



As dinitranisic acid had given Ittner and one of us § a comparatively stable compound, when treated with sodic ethylate, we at first tried to prepare similar compounds from it and other sodic alkylates; but a few experiments convinced us that the products from these reactions were too unstable for our purpose. Our attention was then called by one of our associates in this Laboratory to the red substance formed by the action of sodic methylate on picrylchloride, and this has led to the discovery and analysis of the following compounds:—

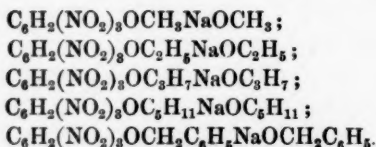
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\* Am. Chem. Journ., XIX. 199.

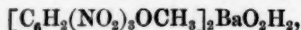
† Lobry de Bruyn and Van Leent, Rec. Trav. Chim. Pays Bas, XIV. 150.

‡ Van Leent, Ibid., XV. 89.

§ Jackson and Ittner, Am. Chem. Journ., XIX. 210.



To which should be added a substance formed by the action of aqueous baric hydrate on a solution of trinitranisol in methyl alcohol, probably



which was also obtained crystallized with ten molecules of water. All of these substances have vivid red colors, and are decomposed by an acid, or more slowly by water, giving the picric ether. They are remarkably stable for compounds of this class.

The study of these substances has thrown some light on their constitution. The only published theory about bodies of this class is the suggestion made by the lamented Victor Meyer in his first paper\* on this subject, that they might be formed by the replacement of one of the atoms of hydrogen on the benzol ring by potassium or sodium. According to this view our methyl compound would be formulated as follows:  $C_6HNa(NO_2)_3OCH_3CH_3OH$ ; that is, it would contain a molecule of methyl alcohol of crystallization. Lobry de Bruyn† has brought forward an almost, if not absolutely, conclusive argument against this theory in his observation that sodium does not act on trinitrobenzol, even when in a boiling xylol solution, and therefore that trinitrobenzol cannot contain an atom of hydrogen which can be replaced by sodium. Our work described in this paper furnishes two arguments which confirm that of Lobry de Bruyn. First, it has shown that all of the substances analyzed so far contain according to this theory one molecule of alcohol of crystallization, while the salt without alcohol of crystallization predicted by it ( $C_6HNa(NO_2)_3OCH_3$ , for instance) has never been obtained. Second, we have found that the methyl compound  $C_6H_2(NO_2)_3OCH_3NaOCH_3$  can be heated to  $130^\circ$  without loss of weight, which could not have been the case had it contained methyl alcohol of crystallization, as is required by this theory. While neither of these arguments is so convincing as that derived by Lobry de Bruyn from the action of metallic sodium, they give it a strong confirmation,‡ and we are satisfied therefore that Victor Mey-

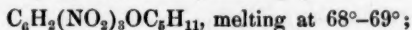
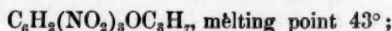
\* Ber. d. chem. Ges., XXVII. 3153.

† Rec. Trav. Chim. Pays Bas, XIV. 89.

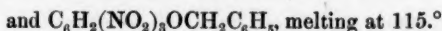
‡ Ittner and one of us (Am. Chem. Journ., XIX. 212) observed that the compound  $C_6H_2(NO_2)_3OCH_3COONaNaOC_2H_5$  gave off alcohol when heated, but this obser-

er's theory in regard to these bodies should be abandoned, and that they should be considered as formed by the addition of the sodic alcoholate to the aromatic nitro compound. Whether the alcoholate is added to the carbon of the benzol ring or to the nitro group cannot be determined with our present knowledge, but possibly a way has been opened to decide this question by the discovery of the addition compounds formed from quinone and potassic ethylate or hydrate described by Astre,\*  $C_6H_4O_2KOC_2H_5$  and  $C_6H_4O_2KOH$ , and that from chloranil and sodic methylate,  $C_6Cl_4O_2NaOCH_3$ , obtained by H. A. Torrey and one of us.† These substances, by their striking colors, their formulas, mode of formation, and slight stability, seem to be related to the class of compounds discussed in this paper, and, if this connection can be proved, would show that the alcoholate is added to carbon and not to the nitro group. In continuing work in this direction an attempt will be made to find such substances not derived from quinones, as in quinones a special method of attachment of sodic alcoholate is possible, forming the hemiacetals. This line of work will be pursued in this Laboratory during the coming year. It is worth mentioning that Astre independently of Victor Meyer explained the constitution of his compounds by supposing the hydrogen on the quinone ring had been replaced by potassium, thus,  $C_6H_3KO_2C_2H_5OH$ , a hypothesis which is inadmissible, as our derivative from chloranil undoubtedly belongs to the same class, and here ( $C_6Cl_4O_2NaOCH_3$ ) no such arrangement of the atoms is possible. The details of this argument will be found in the paper by H. A. Torrey and one of us,† already mentioned.

By the decomposition of the corresponding colored compounds with an acid the following new picric ethers were obtained:—



this was made from ordinary isoamylalcohol;




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vation is of little weight in favor of the theory, since the substance at the same time underwent a far-reaching decomposition, of which the alcohol may have been a product, instead of being alcohol of crystallization.

\* C. R., CXXI. 530 (1895).

† These Proceedings, XXXIII. 167.

## EXPERIMENTAL PART.

*Action of Sodid Methylate on Picrylchloride.*

When a concentrated solution of picrylchloride in methyl alcohol was mixed with an excess of sodic methylate also dissolved in methyl alcohol, a mass of beautiful scarlet needles was formed immediately; or, if the solution was dilute, these scarlet needles appeared only upon standing. We first prepared the substance for analysis only by washing with water, in which it is but slightly soluble, and drying on a porous plate. The analysis of this preparation is numbered I. A second portion after being washed with water was recrystallized from methyl alcohol, which partially decomposed it, as white plates of trinitranisol could be distinguished mixed with the scarlet prisms of the new body. This impurity was removed by washing with benzol, in which the scarlet compound is nearly insoluble, but the trinitranisol very soluble. This preparation dried *in vacuo* was analyzed with the result numbered II.

The scarlet compound formed according to Clemm,\* when a solution of picrylchloride in methyl alcohol was treated with sodic hydrate, was also prepared, and gave on analysis the result numbered III, which proves that it is identical with the product obtained by the action of sodic methylate.

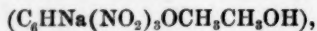
- I. 0.5280 gram of the substance gave, after decomposition with sulphuric acid, 0.1168 gram of sodic sulphate.
- II. 0.3518 gram of the substance gave 0.0857 gram of sodic sulphate.
- III. 0.1680 gram of the substance gave 0.0410 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OCH_3NaOCH_3$	I.	Found. II.	III.
Sodium	7.69	7.17	7.89	7.90

The formula  $C_6HNa(NO_2)_3OCH_3$  requires 8.68 per cent of sodium.

These results indicate that the substance is formed by the addition of one molecule of sodic methylate to one molecule of trinitranisol. The sodic chloride, which must have been the other product of the reaction, was removed by washing with water in the preparation of the substance.

As, according to the theory proposed by Victor Meyer, this substance must contain a molecule of methyl alcohol of crystallization,




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\* Journ. Prakt. Chem., [2], I. 156.

we next studied the effect of heat upon it. A sample dried for twenty-four hours *in vacuo* was heated to 100°–110°. After one hour's heating it had lost 0.0002 gram, and upon further heating remained constant. The heat was then increased to 130°–140°, but even at this temperature there was no loss in weight. In view of this experiment it seems impossible to maintain that the substance contains methyl alcohol of crystallization. When the temperature was raised to 165°, the substance decomposed, as was shown by a change in color.

*Properties of the Addition Product of Trinitranisol and Sodid Methylate.*

— It crystallizes from methyl alcohol (with slight decomposition) in prisms apparently belonging to the monoclinic system, of a beautiful scarlet, or perhaps rather vermilion color with a bronze reflex. It decomposes at about 165°, and, if heated in the free flame, explodes with great violence. In the dry state it is comparatively stable, keeping well even when exposed to the air; but in contact with water it is gradually decomposed, forming trinitranisol, which, if the action is very long continued, passes into picric acid. Methyl alcohol dissolves it, but not without decomposition, as some trinitranisol is found mixed with the crystals obtained from such a solution; it is almost insoluble in benzol. Acids decompose it at once, forming a body, which after recrystallization from alcohol melted at 64° and was therefore evidently trinitranisol; methyl alcohol was also set free, as shown by the odor.

*Action of Ethyl Alcohol on the Addition Product of Trinitranisol and Sodid Methylate.*

This work was undertaken in the hope of deciding whether the addition product contained methyl alcohol of crystallization, as in that case the methyl alcohol must be replaced by ethyl alcohol upon recrystallization from this solvent, whereas, if the second methyl group was not present in alcohol of crystallization, it might either remain in the compound under these conditions, or be replaced by the ethyl group. If, therefore, the methyl compound were unaltered by crystallization from ethyl alcohol, it could not contain methyl alcohol of crystallization. Unfortunately, the experiment showed that the methyl group was replaced by ethyl, and therefore no inference in regard to the constitution of the body could be drawn from this work.

On recrystallizing the methyl compound from ethyl alcohol a substance was obtained closely resembling the original methyl compound in color, crystalline form, and properties, but which gave the following result on analysis after having been dried *in vacuo*: —



0.3012 gram of the substance gave 0.0681 gram of sodic sulphate.

	Calculated for $C_6H_5(NO_2)_3OC_2H_5NaOC_2H_5$ .	Found.
Sodium	7.23	7.32

This result seems to indicate that the body is the ethyl compound, but is not conclusive, as the difference between the percentages of sodium in the methyl and ethyl compounds is only 0.46 per cent, and the experimental error may well reach or even exceed this amount in the case of compounds which are so hard to purify on account of their instability. But we do not have to depend on the analysis in this case, as upon decomposing the substance with an acid, and recrystallizing the product from alcohol long nearly colorless needles were obtained, which melted at  $78^\circ-79^\circ$ , and were, therefore, the ethyl ether of picric acid. We hope that further experiments in this direction will be tried in this Laboratory during the coming year.

An attempt to make this ethyl compound direct from sodic ethylate and picrylchloride did not lead to the desired result; a mass of red crystals was formed to be sure, but these dissolved, when treated with water to wash out the sodic chloride, giving a red solution, which gradually turned yellow, and then deposited needles of the ethyl picrate.

*Action of Sodic Propylate on Picrylchloride.*

A concentrated solution of picrylchloride in benzol was mixed with an excess of sodic propylate dissolved in a little propyl alcohol; a heavy precipitate of red needles was formed, which was washed thoroughly at first with benzol and afterward with water. It was then dried on a porous plate, and at last at  $110^\circ$ , when the following results were obtained on analysis.

- I. 0.2960 gram of the substance gave on combustion \* 0.4390 gram of carbonic dioxide and 0.1260 gram of water.
- II. 0.6223 gram of the substance gave 0.1235 gram of sodic sulphate.

	Calculated for $C_6H_5(NO_2)_3OC_3H_7NaOC_3H_7$ .	Found.	
		I.	II.
Carbon	40.79	40.45	
Hydrogen	4.53	4.73	
Sodium	6.54		6.44

The formula  $C_6HNa(NO_2)_3OC_2H_5$  requires 36.85 per cent of carbon, 2.73 of hydrogen, and 7.85 of sodium.

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\* The substance was mixed with chromic oxide to decompose the sodic carbonate formed.



*Properties of the Addition Product of Propyl Picrate and Sodio Propylate.* — It resembles the methyl compound closely, but its color is a somewhat lighter red, and it is not quite so stable when exposed to the air. Acids decompose it giving propyl alcohol, recognized by the smell, and the propyl picrate, which has not been described heretofore. Propyl picrate crystallizes in fine nearly colorless needles, melting at  $43^{\circ}$ , and is easily soluble in all the common solvents. If allowed to stand with water or an acid, it is decomposed with the formation of picric acid.

*Action of Sodio Isoamylate on Picrylchloride.*

A benzol solution of picrylchloride was mixed with an excess of sodio isoamylate dissolved in a little isoamyl alcohol, and the amorphous orange precipitate formed was washed thoroughly with benzol and afterward with water, and dried at first on a porous plate finally at  $110^{\circ}$ , when it gave the following results on analysis:—

0.2894 gram of the substance gave 0.0490 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OC_5H_{11}NaOC_5H_{11}$ .	Found.
Sodium	5.62	5.48

The formula  $C_6HNa(NO_2)_3OC_5H_{11}$  requires 7.16 per cent of sodium.

*Properties of the Addition Product from Isoamyl Picrate and Sodio Isoamylate.* — This substance forms an orange amorphous mass, which is decomposed by all the liquids which dissolve it, so that we could not try to crystallize it. It is essentially insoluble in water or benzol. Acids decompose it, setting free amyl alcohol, recognized by its smell, and amyl picrate.

*Isoamyl Picrate,  $C_6H_2(NO_2)_3OC_5H_{11}$ .*

This substance was obtained by the action of an acid on the addition product just described. It was purified by crystallization from alcohol, until it showed the constant melting point  $68^{\circ}$ – $69^{\circ}$ , when it was dried *in vacuo*, and analyzed with the following result:—

0.1311 gram of the substance gave on combustion 0.2117 gram of carbonic dioxide and 0.0558 gram of water.

	Calculated for $C_6H_2(NO_2)_3OC_5H_{11}$ .	Found.
Carbon	44.14	44.02
Hydrogen	4.34	4.73

Isoamyl picrate crystallizes from alcohol in nearly colorless hexagonal plates, which melt at  $68^{\circ}$ – $69^{\circ}$ . It is decomposed by standing with water or acids, but in this respect is much more stable than propyl picrate.

*Action of Sodid Benzylate on Picrylchloride.*

When picrylchloride in benzol solution was treated with an excess of sodid benzylate, a mass of beautiful red needles was formed, which, after washing thoroughly with benzol and water, was dried on a porous plate, and afterward at  $110^{\circ}$ , and analyzed with the following result:—

0.3125 gram of the substance gave 0.0470 gram of sodid sulphate.

	Calculated for $C_6H_2(NO_2)_3OC_7H_7NaOC_7H_7$ .	Found.
Sodium	5.12	4.87

The formula  $C_6HNa(NO_2)_3OC_7H_7$  requires 6.74 per cent of sodium.

*Properties of the Addition Product of Benzyl Picrate and Sodid Benzylate.*—This substance crystallizes in red needles of a somewhat lighter shade than the propyl compound, and shows a distinct fluorescence. It is also more stable than the propyl compound, since a sample of it stood exposed to the air in a watch glass for some months without any visible change. Water decomposes it, but much more slowly than the other compounds of this class. In this decomposition, as well as in that by an acid, the principal products are benzyl alcohol and the benzyl picrate.

*Benzyl Picrate,  $C_6H_2(NO_2)_3OC_7H_7$ .*

This substance, prepared by the action of an acid on the addition product just described, was purified by recrystallization from alcohol, until it showed the constant melting point  $115^{\circ}$ , when an analysis gave the following result:—

0.3828 gram of the substance gave on combustion 0.6805 gram of carbonic dioxide and 0.1090 gram of water.

	Calculated for $C_6H_2(NO_2)_3OC_7H_7$ .	Found.
Carbon	48.90	48.48
Hydrogen	2.82	3.16

Benzyl picrate crystallizes from alcohol, in which it is difficultly soluble, in nearly colorless plates, melting at  $115^{\circ}$ . It is gradually decomposed by acids, forming picric acid.

*Action of Baric Hydrate on Picrylchloride, or on Trinitranisol in Methyl Alcoholic Solution.*

When a concentrated solution of picrylchloride in methyl alcohol was treated with an excess of an aqueous solution of baric hydrate, a dense mass of red crystals was formed, which were collected, and washed with water as quickly as possible to prevent the formation and precipi-

tation of baric carbonate from the excess of baric hydrate. The crystals were then dried on a porous plate. Trinitranisol dissolved in methyl alcohol gives the same compound, when treated with aqueous baric hydrate, and as thus a purer product was obtained, we prepared most of our material in that way. Analysis of the air-dried substance gave the following result:—

0.8154 gram of substance gave 0.2394 gram of baric sulphate.

	Calculated for $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_3]_2\text{BaO}_2\text{H}_2 \cdot 10 \text{ H}_2\text{O}$	Found.
Barium	16.37	17.26

As this indicated that the substance contained water of crystallization, its behavior when heated was studied.

- I. 0.7733 gram of the air dried substance lost 0.1622 gram at  $110^\circ$ – $130^\circ$ .
- II. 0.3513 gram of the air dried substance lost 0.0736 gram at  $110^\circ$ – $130^\circ$ .
- III. 0.8206 gram of the air dried substance lost 0.1738 gram at  $110^\circ$ – $130^\circ$ .

	Calculated for $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_3]_2\text{BaO}_2\text{H}_2 \cdot 10 \text{ H}_2\text{O}$	I.	II.	III.
Water	21.50	20.97	20.95	21.17.

- I. 0.4064 gram of the substance dried at  $110^\circ$ – $130^\circ$  gave 0.1504 gram of baric sulphate.
- II. 0.4616 gram of the substance gave 0.1694 gram of baric sulphate.
- III. 0.1296 gram of the substance gave on combustion 0.1201 gram of carbonic dioxide \* and 0.0259 gram of water.
- IV. 0.2654 gram of the substance gave † 31.4 c. c. of nitrogen under a pressure of 753.1 mm. and at a temperature of  $20^\circ.5$ .

	Calculated for		Found.			
	$[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_3]_2\text{BaO}_2\text{H}_2$	$[\text{C}_6\text{H}(\text{NO}_2)_3\text{OCH}_3]_2\text{Ba}$	I.	II.	III.	IV.
Barium	20.85	22.06	21.76	21.58		
Carbon	25.56	27.05			25.26	
Hydrogen	1.83	1.29			2.22	
Nitrogen	12.78	13.53				13.40

\* Chromic oxide was used to decompose the baric carbonate formed. The substance was spread out in a long copper boat, and heated very carefully to avoid explosions.

† The substance was mixed with sand to decompose any baric nitrite which might have been formed.

These results, therefore, do not decide with certainty between the two formulas, for, although the percentage of carbon speaks strongly in favor of  $[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2$ , the determinations of barium agree better with the percentage calculated for the second formula. As the most probable impurity in the substance was baric carbonate, we shall adopt the formula containing baric hydrate provisionally.

*Properties of the Addition Product of Trinitranisol and Baric Hydrate.* — It forms needles of a fine red color verging toward scarlet. When heated to  $110^\circ$ , it loses its water of crystallization, and turns a beautiful dark crimson, but the dried salt absorbs water very eagerly from the air, regaining its scarlet red color. This fact necessitates great care in handling the dried salt during the process of analysis. Part, but not all, of the water of crystallization is given off *in vacuo*. It is insoluble in water. Acids decompose it, giving trinitranisol, but no alcoholic odor was observed.

Calcic hydrate added to a solution of picrylchloride in methyl alcohol gave a red precipitate, but this decomposed almost immediately with formation of trinitranisol. Dinitranisic acid dissolved in methyl alcohol gave a magnificent purple coloration, when treated with aqueous baric hydrate, but the substance formed was very unstable. It is mentioned here, as it forms an additional argument for classing the trinitranisol compounds described in this paper with the colored derivatives of dinitranisic acid discovered by Ittner and one of us.

The work will be continued in this Laboratory.